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A VERSATILE ROUTE TO FUNCTIONALIZED BLOCK COPOLYMERS BY NITROXIDE MEDIATED 'LIVING' FREE RADICAL POLYMERIZATION

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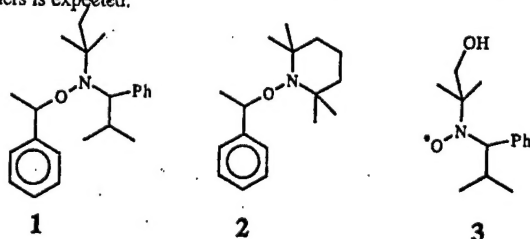
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Introduction

In comparison with other living techniques, two of the unique features of 'living' free radical polymerizations are their compatibility with a wide range of functional groups, coupled with their ability to prepare well defined random and block copolymers from a variety of monomers.¹ We have recently shown that replacement of TEMPO as the mediating nitroxide in 'living' free radical polymerizations by α -hydrogen derivatives leads to monomer selection and functional group compatibility approaching that of ATRP based systems.² The ability of these new alkoxyamines, such as 1, to mediate the homopolymerization of a wide variety of monomers should permit a much greater range of well defined random, block, and star copolymers to be prepared under simplified conditions.

Results and Discussion - Random Copolymers

Initially the random copolymerization of styrene and butyl acrylate mixtures in the presence of 1 and acetic anhydride at 125°C was examined. In contrast to the results obtained with TEMPO, both molecular weight and polydispersity control was excellent, with all molecular weights being within 10% of the theoretical molecular weights and polydispersities between 1.08 and 1.20. Given the control afforded by 1 in the homopolymerization of both styrenics and acrylates, this ability to prepare well-defined random copolymers is expected.



However a more surprising result was obtained when the random copolymerization of styrene and methyl methacrylate was examined. In this case, well defined random copolymers could be obtained up to very high methyl methacrylate ratios (ca. 85%) and only at methacrylate ratios of greater than 90% did the polydispersity become greater than 1.50. Significantly no resonances were observed in the 5.50-6.20 ppm region, characteristic of alkene terminated chains. To better appreciate these results, the polydispersities obtained for the random copolymerization of styrene/butyl acrylate and styrene/methyl methacrylate mixtures initiated by 1 were compared with those for TEMPO based systems, 2. Significantly greater control is observed with 1 compared to TEMPO at essentially all molar ratios and becomes exacerbated at molar percentages of styrene of less than 60% (Figure 1). Similarly the random copolymerization of acrylates and methacrylates, which fails for TEMPO based systems such as 2, was a controlled process in the presence of 1. For example, a mixture of *t*-butyl acrylate (100 equiv.) and methyl methacrylate (100 equiv.) were heated at 125°C in the presence of 1.0 equivalents of 1 and 0.05 equiv. of the free nitroxide 3. The copolymer obtained was shown to be a statistical random copolymer by ¹H NMR and analysis by GPC, $M_n = 22\ 000$ PD. = 1.19, demonstrating that the level of control was similar to that found above for the styrene/methacrylate random copolymers. This was further confirmed by examination of a wide range of copolymer ratios which showed that well defined materials (PD. < 1.35) were obtained up to 80% of methyl

methacrylate and only at higher methacrylate ratios did polydispersities become greater than 1.50.

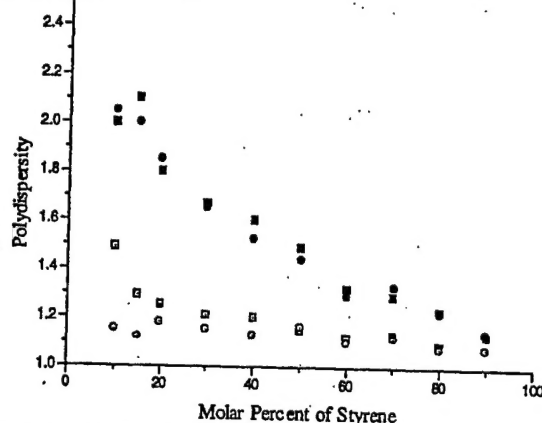


Figure 1. Relationship between polydispersity of the resulting random copolymers and mole percent of styrene in the feed mixture for the copolymerization of (i) styrene and n-butyl acrylate (■), (ii) styrene and methyl methacrylate (●) mediated by TEMPO based systems, 2, compared with (iii) styrene and n-butyl acrylate (○), and (iv) styrene and methyl methacrylate (□) mediated by 1.

Similar control was obtained with other monomers such as acrylamides and acrylonitrile, which clearly demonstrates that an extremely diverse set of well-defined random copolymers can be easily prepared using nitroxide mediated processes.




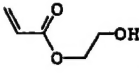
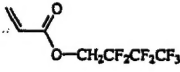
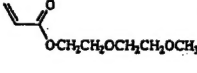
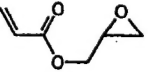
Table 1. Polydispersity and polystyrene equivalent molecular weights, M_n , for the bulk random copolymerization of styrene and a variety of functionalized monomers (200 equiv.) in the presence of 1 at 120°C.

Comonomer	Ratio of Sty/Comonomer	M_n	Polydispersity
	90/10	21 500	1.09
	70/30	22 000	1.12
	50/50	22 500	1.14
	30/70	19 000	1.06
	70/30	20 000	1.1
	50/50	18 000	1.11
	30/70	19 500	1.14
	90/10	19 500	1.09
	80/20	20 000	1.08
	50/50	20 500	1.12
	90/10	19 500	1.07
	70/30	17 000	1.12
	50/50	18 000	1.22

The ability to polymerize functionalized monomers under controlled conditions is a major advantage of 'living' free radical procedures.^{3,4} The demonstrated capacity of 1 to polymerize a wide variety of monomer families suggested that it might also be compatible with reactive functional groups such as carboxylic acids, epoxides, etc. This feature was probed by copolymerizing mixtures of styrene, or butyl acrylate, with a variety of reactive monomer units. As shown in Tables 1 and 2, a high degree of control was maintained over the random copolymerization even in the presence of a significant amount of the reactive monomer unit, ca. 1:1. At low levels of incorporation, ca. <25%, the influence of functionalized monomers on the level of control was negligible. For a range of functional groups, from basic amine, acidic carboxylate, fluorocarbon, to hydrophilic groups low polydispersity, well-defined polymer were obtained. Only at high loading levels (ca. 50%) and in select cases, such as acrylic acid and glycidyl acrylate,

did the polydispersities rise to 1.5-1.55. Similar difficulties in the polymerization of acrylic acid was observed in ATRP procedures by Matyjaszewski where the catalyst is deactivated by the co-ordinating ability of the monomer.⁵

Table 2. Polydispersity and polystyrene equivalent molecular weights, M_n , for the bulk random copolymerization of butyl acrylate and a variety of functionalized monomers (200 equiv.) in the presence of 1 and 3 (0.05 equiv.) at 120°C.

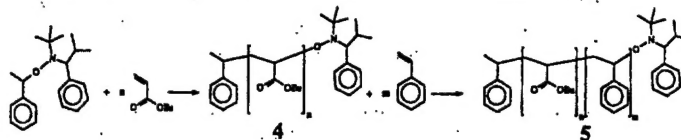
Comonomer	Ratio of Acrylate/Comonomer	M_n	Polydispersity
	90/10	17 000	1.18
	80/20	14 500	1.15
	70/30	16 500	1.13
	50/50	18 000	1.09
	30/70	18 000	1.1
	10/90	17 000	1.15
	95/5	19 500	1.12
	90/10	21 500	1.1
	80/20	22 000	1.26
	50/50	20 000	1.55
	70/30	15 500	1.18
	50/50	14 500	1.19
	30/70	17 000	1.15
	95/5	19 000	1.14
	90/10	18 000	1.19
	50/50	18 000	1.30
	90/10	19 500	1.12
	50/50	19 000	1.25
	90/10	20 000	1.17
	80/20	19 000	1.15
	50/50	17 000	1.35
	95/5	20 000	1.16
	90/10	21 000	1.18
	80/20	23 000	1.18
	50/50	28 000	1.52

Block Copolymers

The presence of dormant initiating centers at the chain end/s of linear polymers prepared by both nitroxide mediated and ATRP procedures provides unique opportunities for the preparation of block copolymer structures and this feature has been exploited by numerous groups.⁶ While the block copolymers available from 'living' free radical procedures may not be as well defined as the best examples available from anionic techniques, they have the advantage of greater availability and a significantly greater tolerance of functional groups.

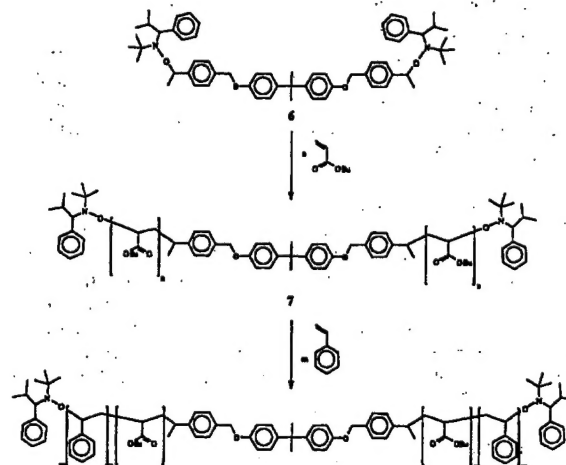
In exploiting these opportunities, nitroxide mediated systems has lagged behind ATRP based systems, primarily due to the more limited choice of monomer units that could be efficiently homopolymerized. The ability of 1 to overcome this limitation opens up the possibility of preparing a wide range of block copolymer structures using nitroxide mediated procedures. Initially, an alkoxyamine functionalized poly(*n*-butyl acrylate) block, 4 ($M_n = 7\ 800$, PD. = 1.08), was initially grown and then used to polymerize 200 equivalents of styrene in the presence of acetic anhydride (1.0 equivalents) at 123°C under argon for 8 hours. This resulted in 92% conversion and gave the block copolymer, 5, analysis of which revealed the expected increase in molecular weight ($M_n = 28\ 000$, PD. = 1.09), while the polydispersity remained very low and there were no detectable amount of unreacted starting poly(acrylate) block

as analyzed by a combination of GPC and h.p.l.c. techniques. This block copolymer formation proved to be a general procedure and permitted a wide compositional range of poly(*n*-butyl acrylate)-*b*-polystyrene block copolymers to be prepared with accurate control of molecular weight up to 200 000 a.m.u. and polydispersities typically in the range of 1.06-1.19 (Scheme 1).



Scheme 1

The preparation of functionalized derivatives of 1 also permits the synthesis of more complex block copolymer architectures. For example, the difunctional initiator, 6, can be readily prepared and a wide variety of ABA triblock copolymers, 8, obtained by initial polymerization of butyl acrylate to give the central B block, 7, followed by polymerization of the two outer polystyrene A blocks (Scheme 2). A number of these samples proved to be interesting functionalized thermoplastic elastomers with novel properties and potential applications.



Scheme 2

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